

BUBBLE FORMATION AND GROWTH

Study of the Boundary Conditions at the Bubble Wall
Through Irreversible Thermodynamics

by

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PREFACE

This quarterly progress report is constituted mainly of the Master thesis submitted by K. R. Chan. It represents the work done during the period of February-May 1965. It is a preliminary study of the boundary conditions at the bubble wall using concepts of irreversible thermodynamics.

In this work the fluxes across the bubble wall were assumed to depend linearly upon the driving forces. This is only a first approximation, as it is known that the relation between the fluxes and the driving forces are non-linear. This assumption leads to an improved set of boundary conditions which contain as a special case the commonly assumed boundary conditions of equilibrium across the wall.

In the next phase of the work, a more exact study of the boundary condition will be made with the goal of determining the non-linear relations between the fluxes and the driving forces.

ABSTRACT

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Growth or collapse of a spherical vapor bubble in a sea of one component inviscid liquid with constant material properties was considered in the absence of force fields. Vapor was assumed to be uniform in temperature. Since mass and heat cross the discontinuity at the phase boundary, a coupling between heat and mass flux is expected with the accompanying discontinuities of temperature and chemical potential. The present study differs from previous works in the literature in its consideration of those non-equilibrium effects with the techniques of irreversible thermodynamics and kinetic theory. A new pair of differential equations to be solved simultaneously for the bubble radius behavior was developed. Improvement over previous works^(7,11,17,19) is expected when the bubble wall velocity reaches a very high value in the order of sonic velocity of the liquid as in the final stage of bubble collapse.

Author

I. INTRODUCTION

The processes in vapor bubble growth and collapse are quite complex, and many simplifications are necessary for analytical solutions. The present study limits itself to a case where the infinite, inviscid, and one-component liquid surrounds a bubble whose shape remains spherical, no body forces are present, and the liquid and vapor properties such as the thermal conductivities (k) specific heats (c_p), and the surface tension (σ) remain constant.

Lord Rayleigh¹ considered the simplest case of a vacuum void collapsing in an incompressible liquid under a constant pressure p_∞ at infinity. The laws of conservation of mass and momentum led to the well-known Rayleigh equation:

$$p_\infty - p(R) = \rho_1 \left[R \frac{d^2 R}{dt^2} + \frac{3}{2} \left(\frac{dR}{dt} \right)^2 \right] \quad (1)$$

where the coordinate origin is at the center of the bubble, R the bubble radius, $p(R)$ the pressure in the liquid at $r = R$, ρ_1 the liquid density. The surface tension effect on pressures across the curved boundary was neglected. (When the void is vacuum, $p(R) = 0$.) Next, by equating the work done on the system when the bubble contracts from an initial radius R_0 to R to the total kinetic energy of the system, he obtained

$$\left(\frac{dR}{dt} \right)^2 = \frac{2}{3} \frac{p_\infty}{\rho_1} \left(\frac{R_0^3}{R^3} - 1 \right) \quad (2)$$

Here (p_∞) can be replaced by $p_\infty - p(R)$ as long as $p(R)$ remains constant. If there is initial pressure p_g^0 inside the bubble and if the

gas is noncondensable obeying the Boyle's law,

$$\left(\frac{dR}{dt}\right)^2 = \frac{2}{3} \frac{p_\infty}{\rho_1} \left(\frac{R_0^3}{R^3} - 1\right) - 2 \frac{p_g^0}{\rho_1} \frac{R_0^3}{R^3} \ln \frac{R_0}{R} \quad (3)$$

If $p_g^0 > p_\infty$ in (3), the bubble will expand.

The possibility of high liquid velocity of order of the velocity of sound near the bubble at low $\frac{R}{R_0}$ as pointed out by Lord Rayleigh led many workers^{2-6,12} in the subsequent period to consider slightly compressible liquid. Gilmore⁶ arrived at an expression for the wall velocity under the same idealizations as in Rayleigh's solution except the assumption that the liquid is slightly compressible:

$$\left(\frac{R_0}{R}\right)^3 = \left(1 - \frac{dR}{dt}/C\right)^4 \left\{ 1 + \frac{3}{2} \frac{\int_1^{\frac{dR}{dt}} \left(\frac{dR}{dt}\right)^2}{[p_\infty - p(R)]} \right\} \quad (4)$$

where C is the velocity of sound in liquid at the wall. When the liquid is incompressible (i.e., $\frac{dR}{dt}/C = 0$), (4) reduces to (2). The comparison between (2) and (4) is shown in Fig. 1. Fig. 2 shows effect of $p_\infty - p(R)$ varying from 0.2 atm up to 3 atm. (P. 15 of Ref. 6).

The divergence between the compressible and incompressible theory becomes more pronounced at higher wall velocities as expected. When incompressible theory predicts Mach number 1, the compressible theory predicts only 0.65. Unfortunately, there was no experimental data to compare the two theories with what really happens near the final stage of collapse.

Later Hickling and Plesset¹² considered the effects of non-condensable gas inside the bubble whose pressure obeys $p_g = \rho_g^x$ where $1 \leq x \leq 1.4$.

Numerical solutions were presented for the pressure and velocity fields as function of time in graphs, from the start of collapse to the beginning of the first rebound.

In all the works thus far discussed, the assumption of no mass flux at the wall and constant temperature throughout the system made the heat transfer considerations unnecessary. In reality, the void is neither vacuum nor filled with non-condensable gas, but contains the vapor phase of the same liquid which either evaporates or condenses at the bubble wall. Expansion or contraction of the vapor phase is coupled to the motion of the liquid sea. If the void were vacuum, the velocity at the bubble wall would approach infinity monotonically as the bubble nears the complete collapse. On the other hand, the bubble with non-condensable gas will never completely collapse, but will oscillate between the maximum and minimum radii indefinitely, unless the kinetic energy dissipates in the medium by viscosity.

A vapor bubble will approximate the extremes of vacuum void and non-condensable gas bubble under certain conditions. Suppose the liquid has an infinite thermal conductivity. Then, the vapor pressure inside the bubble will remain constant during the collapse due to the prevailing isothermal condition. This is when $p(R)$ in (2) is non-zero and constant. Suppose, on the other hand, the liquid has zero conductivity, then no condensation or evaporation can take place, and the vapor bubble will oscillate between two diameters endlessly. Since fluids have finite thermal conductivities, the bubble wall temperature will inevitably rise with a finite rate of condensation. If the temperature rise

becomes high enough to induce a vapor pressure higher than p_1 , then the bubble may stop collapsing and reverse the direction and repeat oscillation toward the complete collapse.

Zwick and Plesset⁷ solved the problem allowing mass flux at the bubble wall assuming (a) constant densities for both vapor and liquid, (b) the vapor pressure p_g to be the saturation pressure corresponding to the instantaneous wall temperature T_R , (c) the liquid and vapor initially at thermal equilibrium with $T = T_0$, (d) constant p_1 , and (e) $p_g - p_1(R) = \frac{2\sigma}{R}$. They first solved¹⁷ the energy equation for the temperature distribution in the liquid with the boundary conditions $T = T_0$ at $r = \infty$ and $\left[k\left(\frac{\partial T}{\partial r}\right)\right]_{r=R} = h_{fg} \int_g \frac{dR}{dt}$ at $r = R$. Then, the pressure variation inside the bubble p_g was expressed in terms of T_R by assuming an approximate Clausius-Clapeyron relation. The known p_g was substituted into the Rayleigh equation. The resulting equation is a nonlinear, integro-differential equation and was integrated numerically for one set of initial conditions. (The results are reproduced in Fig. 3.) The comparison with the Rayleigh solution indicates that the solution with vapor heating practically coincides with the former except near the final stage of collapse where the vapor heating has a slight retarding effect on the collapse. Not only the lack of generality but also the absence of matching experimental data leaves the solution without confirmation as to the degree of validity.

Plesset and Zwick^{7,17} obtained analytical solutions to the previously mentioned integro-differential equation for the case of expanding bubble by subdividing the period of expansion into several regimes and

by utilizing the simplifications possible in each regime. For the asymptotic stage of growth ($R \gg R_0$), they derived

$$h_{fg} \rho_g \frac{dR}{dt} = \sqrt{3} \frac{k(T_o - T_{sat})}{\sqrt{\pi \alpha t}} \quad (5)$$

where α is the thermal diffusivity of liquid and T_{sat} the saturation temperature corresponding to p_o .

Forster and Zuber^{19,20} formulated vapor bubble growth problems independently but along the same way as Plesset and Zwick did. The result differed from (5) only by a factor of constant, i.e., $\frac{\pi}{2}$ in place of $\sqrt{3}$ in (5). Bosnjakovic¹⁴ much earlier solved the bubble growth problem totally neglecting the dynamics and assuming evaporation across a stationary interface and arrived at a result which differs from (5) in that his result had factor 1 in place of $\sqrt{3}$ of (5).

Both groups, Plesset, et al. and Forster, et al., showed satisfactory comparisons between their theories and Dergarabedian's experimental data on bubble growth.¹⁸ Thus, the asymptotic growth rate of the bubble seems to be well established by eq. (5) and to be influenced mostly by the heat transfer condition rather than inertial effects of the liquid.

Many other groups^{22,26,28} considered similar vapor growth problems, and their basic approach differed little from those already mentioned.

In summary, Gilmore modified the Rayleigh solution for collapse of a bubble by allowing a slight compressibility to exist in the liquid. Hickling and Plesset further allowed a non-condensable gas to exist within the bubble whose pressure is variable. Zwick and Plesset neglected

the liquid compressibility but allowed the condensation to take place at the wall and assumed p_g to be the saturation pressure corresponding to the instantaneous bubble wall temperature. The asymptotic growth rate of a vapor bubble as formulated by Plesset and Zwick and Forster and Zuber seems to match well with the experimental data by Dargatzis.

When mass and heat cross discontinuous phase boundaries, coupling between heat and mass fluxes is expected with the accompanying discontinuities of temperature and chemical potential at the boundary. Since the phase boundary is a non-equilibrium region, the equilibrium relationships among the thermodynamic variables, such as Clausius-Clapeyron relation, are only approximations. The higher the fluxes, the less valid the equilibrium approximation becomes. Furthermore, the equilibrium vapor pressure across a curved phase boundary is different from the saturation pressure corresponding to the same temperature at wall. The present study reformulates the boundary conditions taking into account the flux coupling and discontinuities in temperature as well as chemical potential by utilizing the techniques of irreversible thermodynamics and kinetic theory.

II. COUPLED-FLOW EQUATIONS AT THE PHASE BOUNDARY

II.1 Thermodynamics of Irreversible Processes

For a reversible process the second law states that

$$\sum dS = 0 \quad (1)$$

where $\sum dS$ is the entropy increment of all systems affected by the process. Reversible processes are infinitely slow processes. Processes which occur at finite rates are irreversible, and

$$\sum dS > 0 \quad (2)$$

for such processes between equilibrium states.

For a single irreversible process such as heat transfer, a conductivity coefficient (thermal conductivity in case of heat transfer) and the corresponding potential difference or gradient are sufficient to determine the flow. When two or more irreversible processes occur simultaneously in the same system, in general, they will not be independent of one another's potential differences, unless they are of different tensorial character. In bulk flow of one-component liquid system, however, the heat transfer is dependent on the temperature gradient in the direction of heat flow alone but independent of the pressure gradient in any direction.

When irreversible processes are proceeding at finite rate, the question arises whether the usual thermodynamic variables and properties are still valid. If it is possible to make subdivisions of non-equilibrium regions large enough to contain many molecules (and hence to have macroscopic properties) and yet small enough so that the gradients within a given portion are small, then the finally measured

properties after a "local isolation" are assigned to the original system. (30, Art. 49-1) There may be regions of high gradient where isolation process is not valid, but if the region contains negligible mass, such region can be treated as a discontinuity. It has been shown that the validity of assigning thermodynamic variables when transport processes are occurring is in the range of linear-rate-laws. (32)

Let the regions I and II, each in equilibrium if isolated, but not in mutual equilibrium when in communication, be connected through

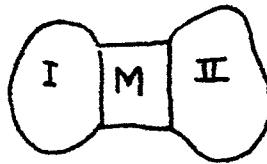


Figure 4. Quasi-static Regions I and II Communicating Through Non-equilibrium Region M

region M. An irreversible rate process then will begin. The entropy production for the whole system will be

$$dS_I + dS_M + dS_{II} > 0.$$

The change of entropy of a homogeneous part like I or II or of any piece in M small enough to be approximately homogeneous is given for simple systems by the Gibbs equation

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \sum_i \frac{\mu_i}{T} dn_i \quad (3)$$

where T is the inverse of temperature; μ_i the chemical potential of component i .

For the calculation of the entropy production in a thin layer of the nonequilibrium region M over either face of which the values of all intensive properties are uniform, one could substitute equilibrium regions I and II on either side without altering the process in the layer, provided that the equilibrium regions had the same values of all intensive properties as those at the face of the layer. Then, the resultant entropy production is generally

$$\dot{S} = \sum_i J_P d\zeta_P \quad (4)$$

where J_P is a flux and $d\zeta_P$ is a differential of a potential which is called force. J_P is defined by

$$J_P = -\dot{P} \quad (5)$$

where \dot{P} denotes the time rate of change of any extensive property of a quasi-static region, and J_P is positive when directed outward from that region. If each flux is linearly dependent on forces, each flux may be written on phenomenological grounds

$$J_i = \sum_j L_{ij} d\zeta_j \quad (6)$$

in which $L_{ij} = \left(\frac{\partial J_i}{\partial \zeta_j} \right)_{\text{all } d\zeta \text{'s} = 0 \text{ except } d\zeta_j}$. This statement is the so-called phenomenological equation for flux J_i . The "conductivities" L_{ij} are independent of any of the gradients and are fixed by the intensive state properties. The development of thermodynamics of linear irreversible processes hinged very much on the Onsager reciprocal relation. This principle says that the matrix of coefficients L_{ij} of set of equations like (6) in which conjugate pairs J_i and $d\zeta_i$ are

identified through expression (4) for the rate of entropy production is symmetrical. That is

$$L_{ij} = L_{ji} \quad (7)$$

II.2 Bubble Model for the Determination of Entropy Production at the Phase Boundary

One can imagine a thin spherical shell M of negligible mass which contains the vapor-liquid phase boundary and has uniform intensive properties on each side, i.e., vapor side and the liquid side; then substitute quasi-static regions I and II each of which has the same value of intensive phase properties as those at the face of the shell and has infinite conductivities as shown in Figure 5.

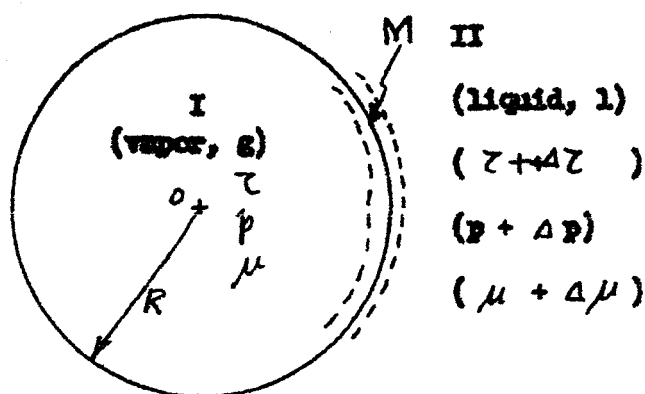


Figure 5. Bubble Model

As shown in Figure 5, the discontinuities in temperature ΔT , chemical potential $\Delta \mu$, and pressure Δp are assumed to exist. In equilibrium, ΔT and $\Delta \mu$ will become zero, but Δp will be $-\frac{2\sigma}{R_0}$ due to the curvature of the bubble wall. When there is large mass flux, Δp will not be equal to $-\frac{2\sigma}{R}$ but will contain additional terms due to the momentum

change when the vapor hits the liquid surface at finite speed. Thus, if we assume negligible vapor velocity,

$$\Delta p \approx -\frac{2\sigma}{R} + \frac{1}{2} \rho_I \left(\frac{dR}{dt}\right)^2 \quad (8)$$

The discontinuities $\Delta\tau$ and $\Delta\mu$ are assumed to be small enough to justify the usage of the Onsager relation.

For region I,

$$\dot{S}_I = \tau \dot{U}_I + p\tau \dot{V}_I - \mu\tau \dot{n}_I. \quad (9)$$

Also define J_{qI} such that

$$\dot{U}_I = h_I \dot{n}_I + J_{qI} - p\dot{V}_I. \quad (10)$$

For region M, the surface mass is negligible, and its energy can only be changed adiabatically and reversibly. Therefore,

$$\dot{S}_M = 0. \quad (11)$$

For region II, equations analogous to (9) and (10) result:

$$\begin{aligned} \dot{S}_{II} &= (\tau + \Delta\tau) \dot{U}_{II} + (p + \Delta p) (\tau + \Delta\tau) \dot{V}_{II} \\ &\quad - (\mu + \Delta\mu) (\tau + \Delta\tau) \dot{n}_{II}, \end{aligned} \quad (12)$$

and

$$\dot{U}_{II} = h_{II} \dot{n}_{II} + J_{qII} - (p + \Delta p) \dot{V}_{II}. \quad (13)$$

In our model, since both regions I and II are assumed to be uniform in temperature, the J_{qI} and J_{qII} can be interpreted as heat which must be rejected to imaginary reservoirs each at (τ) and $(\tau + \Delta\tau)$ for mass entering each region I and II in order to keep each region at the respective temperatures. In real fluid, since the fluid has finite conductivities, J_q 's will be transferred by ordinary conduction

heat, $h \frac{\partial T}{\partial x}$. Since the rate at which heat is conducted into the vapor is usually several orders of magnitude smaller than that for the liquid, J_{qI} will be neglected; we shall call J_{qII} just J_q . Thus, in an isothermal process ($\Delta T = 0$), J_q/\dot{n}_{II} would be the latent heat of vaporization or condensation depending on the direction of the mass flux.

The total entropy production is simply the sum of (9), (11), and (12):

$$\begin{aligned} \dot{S} = & \tau \dot{U}_I + (p\tau) \dot{V}_I - (\mu\tau) \dot{n}_I \\ & + (\tau + \Delta\tau) \dot{U}_{II} + (p + \Delta p)(\tau + \Delta\tau) \dot{V}_{II} - (\mu + \Delta\mu)(\tau + \Delta\tau) \dot{n}_{II} \end{aligned} \quad (14)$$

By the conservation of mass,

$$-\dot{n}_I = \dot{n}_{II} = J_n. \quad (15)$$

Introducing (10), (13), and (15) with $J_{qI} = 0$ into (14),

$$\begin{aligned} \dot{S} = & (-h_I J_n + h_{II} J_n + J_q) \tau \\ & + h_{II} J_n \Delta\tau - (\mu \Delta\tau + \tau \Delta\mu) J_n + J_q \Delta\tau \end{aligned} \quad (16)$$

The first term on the right side of (16) becomes zero by the first law applied to a control volume surrounding the open region M. The second and the third terms can be simplified using the definition $\mu = h - s/\tau$.

$$\begin{aligned} & h_{II} J_n \Delta\tau - (\mu \Delta\tau + \tau \Delta\mu) J_n \\ = & h_{II} J_n \Delta\tau - \left\{ (h_{II} - \frac{s_{II}}{\tau}) \Delta\tau + \tau \left[h_{II} \right] - \tau \left[\Delta \left(\frac{s_{II}}{\tau} \right) \right] \right\} J_n \\ = & J_n \left[\frac{s_{II}}{\tau} \Delta\tau - \Delta h_{II} + \tau \Delta \left(\frac{s_{II}}{\tau} \right) + \Delta s_{II} \right] \\ = & J_n \tau (-\Delta h_{II} + \Delta s_{II}/\tau) = -J_n \tau (\Delta\mu)/\tau \end{aligned} \quad (17)$$

Here, "d" has been used as the differential "d." Finally, we have

$$\dot{S} = J_q \Delta\tau - J_n \tau (\Delta\mu)_\tau \quad (18)$$

$(\Delta\mu)_\tau$ means the chemical potential difference evaluated at the single temperature τ prevailing in the vapor region; that is, in $(\mu_{II} - \mu_I)$ μ_{II} is also evaluated at τ rather than at $(\tau + \Delta\tau)$. Further interpretation follows in II.4.

II.3 The Phenomenological Equations

By equations (6) and (18), one can write

$$J_q = L_{qq} \Delta\tau - L_{qn} \tau (\Delta\mu)_\tau \quad (19)$$

$$J_n = L_{nq} \Delta\tau - L_{nn} \tau (\Delta\mu)_\tau \quad (20)$$

By eliminating $\tau (\Delta\mu)_\tau$ from the equations (19) and (20),

$$J_q = \lambda J_n + L_k \Delta\tau \quad (21)$$

$$\text{where } \lambda = \frac{L_{qn}}{L_{nn}} = (h_I - h_{II}) \Delta\tau = 0, \quad (22)$$

because $(J_q) \Delta\tau = 0 = (h_I - h_{II}) \Delta\tau = 0 J_n$, and

$$L_k = L_{qq} - \frac{L_{qn} L_{nq}}{L_{nn}}. \quad (23)$$

Equation (20) may be written in the form

$$J_n = \frac{L_{nq}}{L_{nn}} L_{nn} \Delta\tau - L_{nn} \tau (\Delta\mu)_\tau. \quad (24)$$

By the Onsager reciprocal relation,

$$J_n = \lambda L_{nn} \Delta\tau - L_{nn} \tau (\Delta\mu)_\tau \quad (25)$$

If L_k and L_{nn} are determined in terms of known variables, all other constants L_{qn} and L_{nq} will also be known by (22), (23), and the Onsager relation.

II.4 Interpretation of $(\Delta\mu)_T$

Figure 6 shows an isotherm at T on a $\mu - p$ diagram. The point c is located corresponding to p_g of vapor region and the point a corresponding to the liquid pressure ($p_g + \Delta p$). p_{go} is defined as the pressure of the vapor bubble which would exist in equilibrium with the liquid at a . Then,

$$\mu_g - \mu_l = \mu_c - \mu_b = \int_{p_{go}}^{p_g} v_g dp.$$

If $v_g \approx \text{const}$ between p_{go} and p ,

$$(\Delta\mu)_T = (\mu_l - \mu_g)_T = v_g (p_{go} - p_g). \quad (25)$$

From the figure

$$p_{go} - p_g = [p_{go} - (p_g + \Delta p)] - [p_g - (p_g + \Delta p)].$$

By (8)

$$p_{go} - p_g = \frac{2\sigma}{R_0} - \frac{2\sigma}{R} + \frac{1}{2} \rho_g \left(\frac{dR}{dt} \right)^2.$$

Therefore,

$$(\mu_l - \mu_g)_T = 2\sigma v_g \left[\frac{1}{R_0} - \frac{1}{R} + \frac{1}{2} \rho_g \left(\frac{dR}{dt} \right)^2 \right]. \quad (27)$$

Equation (27) is interesting in pointing out the unstable nature of equilibrium of vapor bubble with its liquid. Suppose the radius of the bubble initially at R_0 gets slightly smaller accidentally, then μ_g becomes larger than μ_l , and more vapor escapes into liquid reducing R further. If the radius initially grows slightly larger than R_0 , then $\mu_l > \mu_g$, and more liquid will evaporate making R still larger.

Once mass starts to flow, there will be additional pressure jump across the boundary due to the momentum change in crossing the boundary.

II.5 Determination of the Constants L_k and L_{mn}

The first law applied to the "control volume" containing region N gives

$$\text{(See Article III.3 for a detailed derivation.)} \quad J_q = (h_I - h_{II}) J_n \quad (28)$$

Here, it should be noted that h_I is evaluated at τ and p in region I, while h_{II} is evaluated at $(\tau + \Delta\tau)$ and $(p + \Delta p)$. If we assume h_{II} is a weak function of pressure but a strong function of temperature, h_{II} may be thought of as the sum of two parts,

$$(h_{II})_{at} + \frac{\partial h_{II}}{\partial \tau} \Delta\tau \quad (29)$$

Then, (28) becomes

$$\begin{aligned} J_q &= (h_I - h_{II})_{at\tau} J_n - \frac{\partial h_{II}}{\partial \tau} J_n \Delta\tau \\ \text{or } J_q &= \lambda J_n + \frac{C_p}{\tau^2} J_n \Delta\tau \end{aligned} \quad (30)$$

where $C_p = \frac{dh_{II}}{dT}$.

Comparing (21) with (30), one gets

$$L_k = \frac{C_p}{\tau^2} J_n \quad (31)$$

In terms of ordinary temperature T , (30) becomes

$$J_q = \lambda J_n - C_p J_n \Delta T \quad (32)$$

From (25), when $\Delta\tau = 0$, $(J_n)_{d\tau=0} = -L_{mn} \tau (\Delta\mu)_\tau$, or

$$(J_n)_{d\tau=0} = L_{mn} \frac{v_g}{T} (p_g - p_{g0}) \quad (33)$$

In kinetic theory of perfect gases, ⁽²⁸⁾ the mass of the gas crossing per plane unit area per unit time from one side (Γ_+) is

$$\Gamma_+ = p_g \sqrt{\frac{M}{2\pi RT}} \quad (34)$$

where M is molecular weight, R the gas constant, and T the absolute temperature of the gas. This equation is applied to the evaporation or condensation of a liquid by noting that the equilibrium of a liquid and its vapor must be a dynamic one. The liquid is not changed by the presence of the vapor above it; therefore, its rate of evaporation should not be affected by it. However, the vapor is also condensing, and the equilibrium vapor pressure p_{go} is that pressure of vapor for which the two just balance. If it is assumed that only the fraction α of the total gas molecules which hit the liquid surface condenses on the liquid and $(1 - \alpha)$ rebounds into the gas, the gross rate of evaporation of liquid (Γ_+) must be equal to the rate of condensation (Γ_-) to maintain the equilibrium.

$$\Gamma_+ = p_{go} \sqrt{\frac{M}{2\pi RT}} \quad (35)$$

If Γ_+ is assumed to be independent of presence of its vapor, the net rate of condensation at the bubble wall can be written as

$$J_n = 4\pi R^2 (\Gamma_- - \Gamma_+)$$

If $\alpha = 1$ is assumed,

$$J_n = 4\pi R^2 \sqrt{\frac{M}{2\pi RT}} (p_g - p_{go}) \quad (36)$$

Comparing (33) and (36),

$$L_{mn} \frac{V_g}{T} = 4\pi R^2 \sqrt{\frac{M}{2\pi RT}}$$

$$\text{or } L_{mn} = 4\pi R^2 \rho_g \sqrt{\frac{MP}{2\pi RT}} \quad (37)$$

Finally, we have

$$J_q = (\lambda - C_p \Delta T) J_n \quad (38)$$

$$J_n = 4\pi R^2 \rho_g \sqrt{\frac{M}{2\pi RT}} \left[\frac{-\lambda}{T} \Delta T - \frac{1}{\rho_g} (p_g - p_{go}) \right] \quad (39)$$

$$\text{where } p_g - p_{go} = -2\sigma \left[\frac{1}{R_0} - \frac{1}{R} + \frac{1}{2} \rho_g \left(\frac{dR}{dt} \right)^2 \right].$$

According to (38), J_q exists only if J_n does.

II.6 Concerning p_{go}

The equilibrium vapor pressure at T_g inside the bubble is not the same as the saturation pressure across a plane interface at the same T , but the two are related as (30, Art. 26.2)

$$p_{go} = p_{sat} \exp \left[- \frac{2\sigma}{\rho_l T_g R_0} \right] \quad (40)$$

The exponent for water under normal conditions is in the order of $\frac{10^{-7}}{R}$ where R is in foot (or $\frac{3 \times 10^{-5}}{R}$ if R is in centimeters). Thus, for bubbles in the order of 10^{-5} cm radius, the equilibrium pressure may deviate considerably from the saturation pressure. However, $p_{go} \cong p_{sat}$ will be assumed hereafter.

The variation of the saturation pressure with the temperature may be expressed as (28, p. 29)

$$P_{\text{sat}} = T_g^C \exp \left(B - \frac{A}{T_g} \right) \quad (41)$$

where A, B, and C are the vapor pressure constants of a given substance.

III. THE COMPLETE SET OF EQUATIONS

In the preceding chapter, it was necessary to ignore the bulk motions in both regions I and II and to assume infinite thermal conductivities in order to apply Gibb's equation which is valid between equilibrium states only. In this chapter, the equations of motion and energy will be stated for the incompressible, inviscid liquid with constant properties such as λ , k , σ , and C_p . Temperature gradient within the bubble will be assumed zero. It will be assumed that the temperature initially is uniform everywhere at T_0 , and the pressure at infinity is p_∞ .

III.1 Conservation of Mass

A mass balance at the phase boundary yields (see Figure 5)

$$\rho_g \left[(u_g)_{r=R} - \frac{dR}{dt} \right] = \rho_l \left[(u_l)_{r=R} - \frac{dR}{dt} \right] \quad (1)$$

where u denotes the radial velocity of particles in the spherical coordinate. Neglecting ρ_g/ρ_l compared with unity, (1) becomes

$$\frac{dR}{dt} \sim (u_l)_{r=R} \left[1 - \frac{\rho_g u_g}{\rho_l u_l} \right]_{r=R} \quad (2)$$

The conservation of mass for the incompressible liquid gives

$$R^2 (u_l)_{r=R} = r^2 u_l, \quad (3)$$

or by (2)

$$u_l = \frac{R^2}{r^2} \frac{dR}{dt} \frac{1}{\left(1 - \frac{\rho_g u_g}{\rho_l u_l} \right)_{r=R}} \quad (4)$$

Assuming $\left(\frac{\rho_g u_g}{\rho_l u_l} \right)_{r=R} \ll 1$

$$u_1 = \frac{R^2}{r^2} \frac{dR}{dt} \quad (5)$$

III.2 Conservation of Momentum

The momentum equation

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial r} = - \frac{1}{\rho} \frac{dp}{dr} \quad (6)$$

can be integrated between $r = R$ and $r = \infty$ using (5),

$$p_\infty - (p_g + \Delta p) = \rho_1 R \frac{d^2 R}{dt^2} + \frac{3}{2} \rho_1 \left(\frac{dR}{dt} \right)^2 \quad (7)$$

which is the Rayleigh equation. Assuming $p_{go} \approx p_{sat}$,

$$\Delta p = p_g - p_{go} = p_g - p_{sat},$$

where Δp is implicit in

$$J_n = 4\pi R^2 \rho_g \sqrt{\frac{M}{2\pi R T_{gR}}} \left[-\frac{\lambda}{T_{gR}} \Delta T + \frac{1}{\rho_g} \Delta p \right], \quad (II - 39)$$

$$J_n = -\frac{dn_g}{dt} = -\frac{d}{dt} \left(\rho_g \frac{4}{3} \pi R^3 \right) \quad (8)$$

$$p_{sat} = f(T_{gR}) \quad (II - 41)$$

$$\Delta T = (T_1 - T_g)_R$$

Initial conditions are

$$R = R_{oi} \text{ at } t = 0 \text{ and } T_{gR} = T_o,$$

$$\frac{dR}{dt} = 0 \text{ at } t = 0,$$

$$(p_{go} - p_\infty)_{t=0} = \frac{2\sigma}{R_{oi}}.$$

The dynamics of vapor region will be neglected, the vapor pressure will be assumed uniform always, and $(u_g)_R \ll (u_1)_R$ also will be assumed.

III.3 Energy Equation

The energy equation applied to liquid region $R < r < \infty$,

$$\frac{\partial T_1}{\partial t} + u_1 \frac{\partial T_1}{\partial r} = \left(\frac{\partial^2 T_1}{\partial r^2} + \frac{2}{r} \frac{\partial T_1}{\partial r} \right) \quad (9)$$

requires the initial condition and two boundary conditions.

Initial condition: $T = T_0$ everywhere

Boundary conditions: $T_1 = T_0$ at $r = \infty$

$$4\pi R^2 k \left(\frac{\partial T_1}{\partial r} \right)_{r=R} = J_q \quad (10)$$

$$J_q = J_n (\lambda - c_p \Delta T) \quad (II - 38)$$

$$\Delta T = (T_1 - T_g)_{r=R}$$

In the vapor region, T_g will be assumed uniform.

The energy balance applied to the control volume containing region M without neglecting the kinetic energies is

$$J_q - (p_1 - p_g) 4\pi R^2 \frac{dR}{dt} = \sigma 8\pi R \frac{dR}{dt} - J_n \left[\left(h_1 + \frac{1}{2} u_1^2 \right) - \left(h_g + \frac{1}{2} u_g^2 \right) \right]. \quad (11)$$

Dividing both sides by $4\pi R^2$ and using $(p_g - p) \approx \frac{2\sigma}{R}$,

$$J_q = (h_g^0 - h_1^0) J_n \quad (12)$$

where $h^0 = h + \frac{1}{2} u^2$.

In previous chapters, the kinetic energies have been neglected compared with the enthalpies and the equation (28) of Chapter II.

$$J_q = (h_g - h_1) J_n$$

resulted.

III.4 The Final Set of Equations

Expanding (8),

$$-J_n = \rho_g 4\pi R^2 \frac{dR}{dt} + \frac{4}{3} \pi R^3 \frac{d\rho_g}{dt} \quad (13)$$

If the vapor is assumed to be perfect,

$$\rho_g = \frac{p_g}{R T_g} \quad (14)$$

can be used to further expand (13). Combining (10), (II - 38), and (13) and assuming

$$\rho_g \frac{dR}{dt} \gg \frac{R}{3} \frac{d\rho_g}{dt}, \quad (15)$$

one gets

$$k \left(\frac{\partial T_1}{\partial r} \right)_{r=R} = - \rho_g \frac{dR}{dt} (\lambda - c_p \Delta T) \quad (16)$$

If $\Delta T = 0$ in (16), this is the familiar boundary condition which has been traditionally used for solving the energy equation. With the assumption (15), (II - 39) becomes

$$- \frac{dR}{dt} = \sqrt{\frac{M}{2\pi R T_g}} \left[\frac{1}{\rho_g} \Delta p - \frac{\lambda}{T_g} (T_{1R} - T_g) \right] \quad (17)$$

$$\text{or } -\Delta p = \frac{dR}{dt} \rho_g \sqrt{\frac{2\pi R T_g}{M}} - \rho_g \lambda \left(\frac{T_{1R}}{T_g} - 1 \right) \quad (18)$$

The final version of the set of equations, then, is as follows:

The energy equation

$$\frac{\partial T_1}{\partial t} + \left(\frac{R^2}{r^2} \frac{dR}{dt} \right) \left(\frac{\partial T_1}{\partial r} \right) = \left(\frac{\partial^2 T_1}{\partial r^2} + \frac{2}{r} \frac{\partial T_1}{\partial r} \right) \quad (9)$$

with initial condition

$$T_1(r, 0) = T_0$$

and boundary conditions

$$T_1(\infty, t) = T_0$$

$$\left(\frac{\partial T_1}{\partial r}\right)_{r=R} = \frac{\rho_g}{k} \frac{dR}{dt} [\lambda - c_p(T_{1R} - T_g)]$$

The momentum equation

$$p_\infty = \left[p_g - \frac{2\sigma}{R} + \frac{1}{2} \rho_g \left(\frac{dR}{dt}\right)^2 \right] = \rho_l R \frac{d^2 R}{dt^2} + \frac{3}{2} \rho_l \left(\frac{dR}{dt}\right)^2 \quad (7)$$

$$\text{with } R = R_{oi} \text{ at } t = 0, R_{oi} = \frac{2\sigma}{(p_{sat} \text{ at } T_0 - p_\infty)},$$

$$\frac{dR}{dt} = 0 \text{ at } t = 0.$$

$$p_g = \rho_g R T_g \quad (14)$$

$$p_{sat}(T_g) - p_g = \frac{dR}{dt} \frac{h}{g} \sqrt{\frac{2\pi R T_g}{M}} - \rho_g \lambda \left(\frac{T_{1R}}{T_g} - 1\right) \quad (18)$$

Thus, the four unknowns T_1 , T_g , R , and p_g are theoretically obtainable from the four equations (9), (7), (14), and (18).

IV. CONCLUSIONS AND SUGGESTIONS

A pair of differential equations for the bubble radius $R(t)$ with improved boundary conditions taking into consideration the irreversible coupled flow effects at the phase boundary for a vapor bubble in an infinite sea of one-component, inviscid liquid was developed. The vapor was assumed to be uniform in temperature. The liquid was assumed to have constant properties, such as density (ρ_l), thermal conductivity (k), specific heat (C_p), surface tension (σ), and latent heat of vaporization (λ). Since the coefficient $\sqrt{\frac{M}{2\pi\alpha T}}$ is in the order of 5×10^3 ($\frac{\text{lbm}}{\text{ft}^2 \text{ hr}}$) ($\frac{1}{\text{psi}}$) at boiling under atmospheric conditions, the improvement made here will be significant at high mass flux densities, such as at the final stage of bubble collapse.

The following suggestions are made:

1. Attempt an analytical solution.
2. Obtain numerical solution using the same parameters as in Figs. 1-3, and compare the present solution with the previous ones.
3. Since there is no available data on fast-collapsing vapor bubbles, devise an experimental set-up so that the collapse rate at small $\frac{R}{R_0}$ may be measured. If no practical way can be found for such an experiment, the coupled flow effect should be checked across a flat interface by, for example, quickly pulling a piston in a cylinder filled with liquid and simultaneously measuring J_n and ΔT across the interface.

NOMENCLATURE

α	thermal diffusivity
c_p	specific heat of liquid
h	enthalpy per unit mass
k	thermal conductivity
m	mass
p	pressure
r	radial coordinate with origin at the center of bubble
s	entropy per unit mass
t	time
u	radial velocity of particles
v	specific volume
R	radius of the bubble
S	total entropy
T	temperature
R	universal gas constant
h_{fg} or λ	latent heat of vaporization
ρ	density
μ	chemical potential
σ	surface tension

Subscripts

R	at $r = R$
I or g	inside the bubble
II or l	inside the liquid
∞	at $r = \infty$
sat.	saturation property corresponding to T

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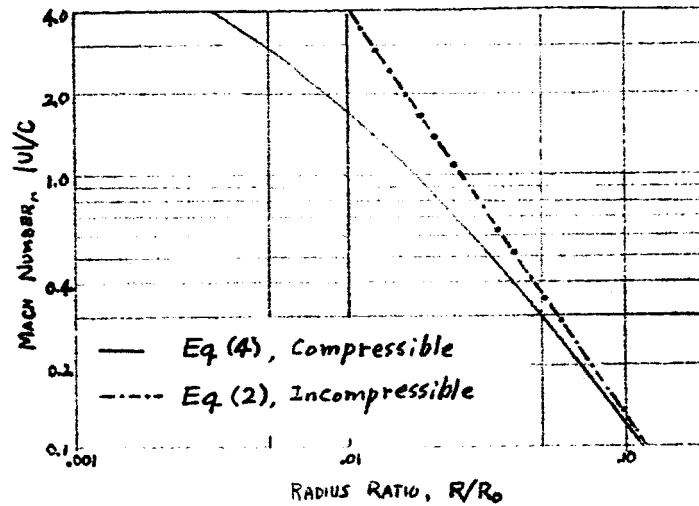


Figure 1. The Theoretical Wall Velocity of a Bubble in Water, Collapsing under a Constant Pressure Difference of 0.517 Atmosphere

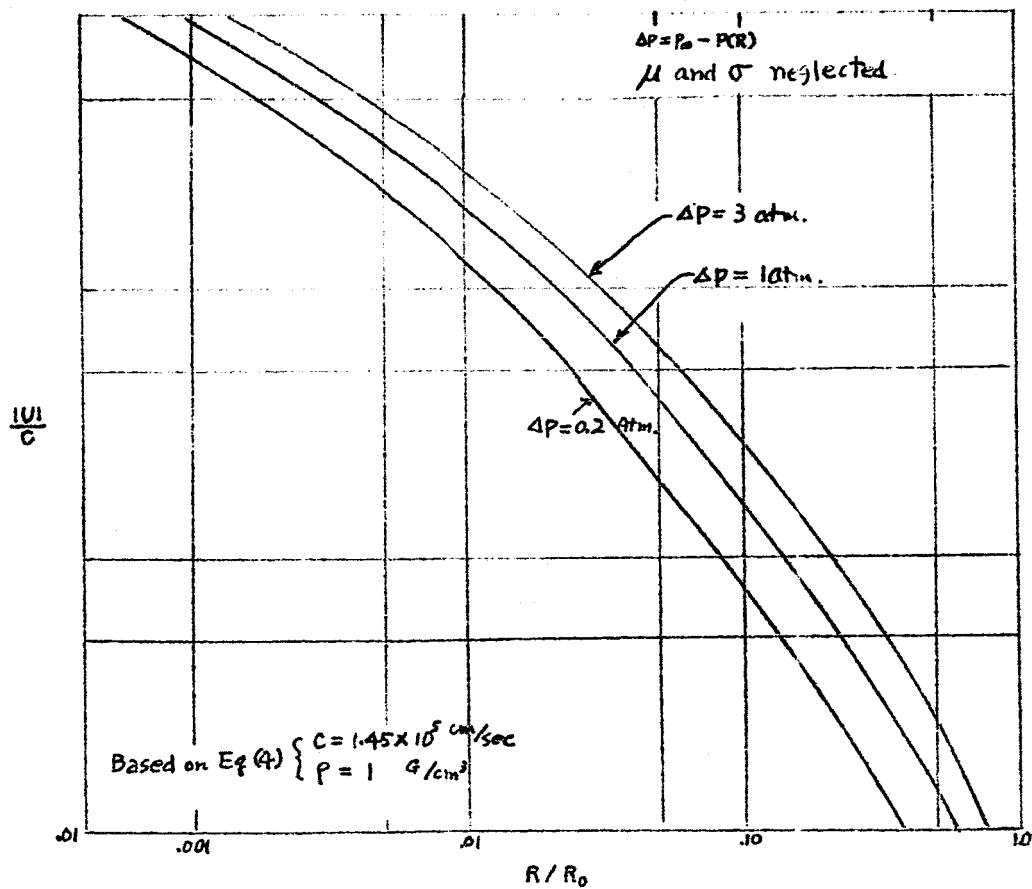


Figure 2. The Theoretical Wall Velocity of Bubbles in Water, Collapsing under Various Constant Pressure Differences

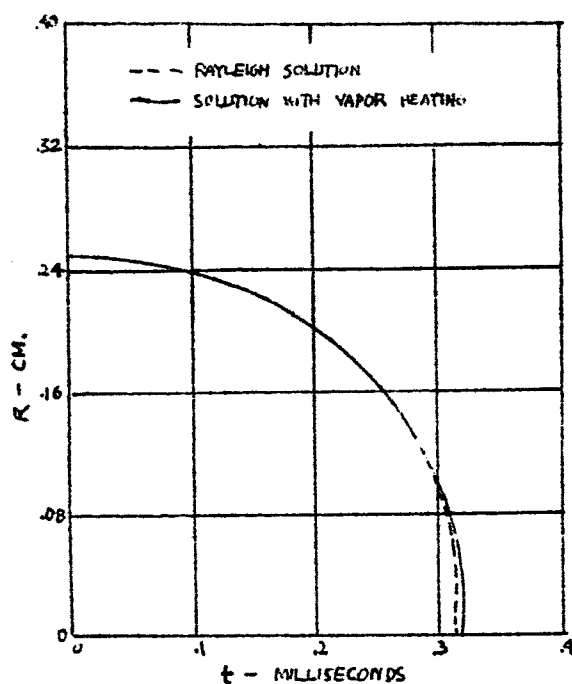
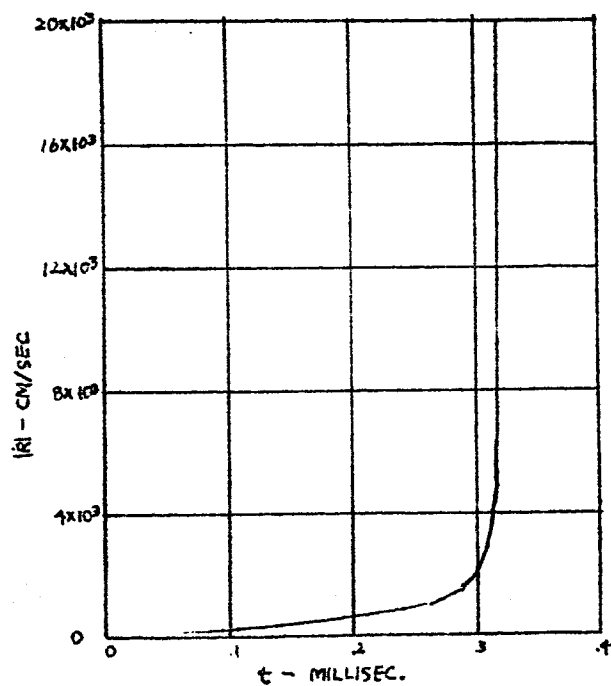
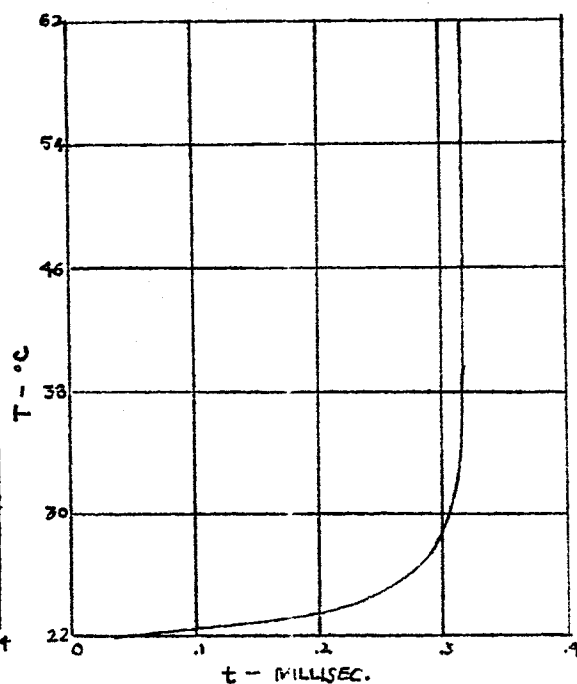


Figure 3. The Radius vs. Time Curve with Initial Radius of 0.25 cm, Water Temperature 22 °C, and P_{∞} at 0.544 atm



Bubble Wall Velocity vs. Time



Bubble Wall Temperature vs. Time

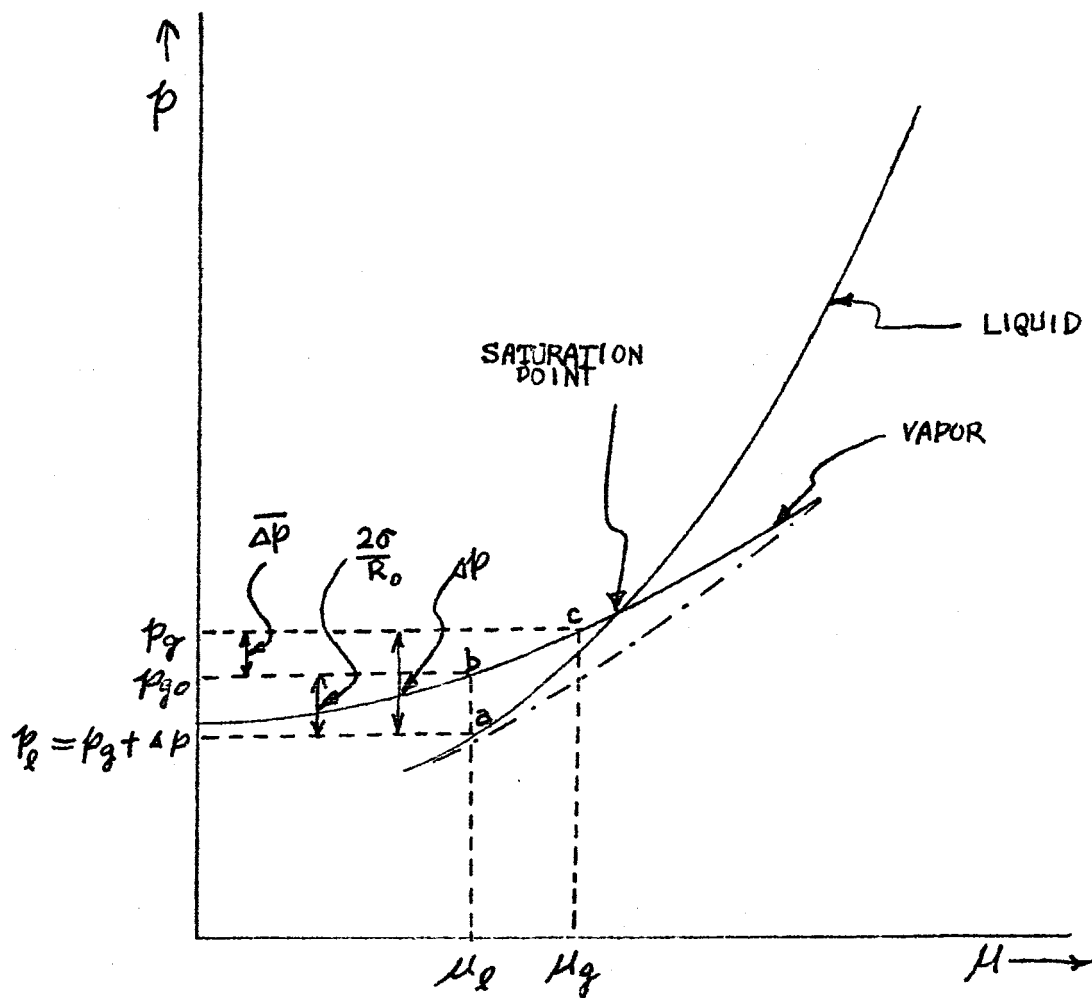


Figure 6. Chemical Potential Isotherm on a $\mu - p$ Plot